The Retentivity of Water by Purified Cotton Cellulose

Dissertation

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By

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The Retentivity of Water by Purified Cotton Cellulose

By HOMER A. HAMM * and W. A. PATRICK †

The adsorption of water vapor by cellulose was studied under conditions to ensure equilibrium. Under these conditions, it was found that cellulose exhibited no hysteresis.

This paper has been presented to the faculty of the Johns Hopkins University as the dissertation of the first-mentioned author in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

Introduction

THE retention of water plays an important rôle in the technology of organic fibrous materials, therefore it has long been the subject of many careful investigations. The present study was undertaken with a view of adding to our information in regard to the mechanism of the retention of water, rather than to supplement our knowledge of the actual amount of water retained under practical working conditions.

We have been guided largely in our approach to this problem by the belief that the presence of small amounts of permanent gases markedly influenced the amount of water retained by porous bodies. The theoretical import of this statement is not fully realized until the important rôle played by the phenomenon of hysteresis in all adsorption studies is remembered. A casual perusal of the adsorption literature is enough to disclose the fact that the occurrence of the phenomenon of hysteresis has served as a basis of dividing the whole consideration of the subject of adsorption into two distinct parts. Zsigmondy [1] was the first to explain hysteresis on the basis of a change in wetting conditions, and this view has served to associate the phenomenon of hysteresis with capillary condensation of the adsorbed vapor. In as much as hysteresis in adsorption measurements does not make its appearance until a considerable amount of vapor has been adsorbed, it is argued that the quantity of vapor adsorbed before the onset of hysteresis must necessarily have been taken up by some other means than by capillary condensation. (See Fig. 1.) The validity of this argument rests upon the reality of the phenomenon of hysteresis. If, for example, it can be shown that hysteresis has its origin in the failure of the experimenter sufficiently to control conditions so as to maintain true equilibrium between vapor and adsorbent, then it becomes necessary to reconsider the entire theoretical aspect of adsorption.

This latter viewpoint has been successfully proven with a large number of artificial inorganic adsorbents such as silica gel, alumina, etc.[2] In other

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words, it has been repeatedly demonstrated that in the case of these various inorganic gels adsorption occurred without any indication of hysteresis. No attempt at a general theory of adsorption has been made, but repeated suggestions of the inadequacy of the present theory of capillarity, or multi-layered adsorption, were always neglected due to the apparent reality of the hysteresis phenomenon in other systems. In the case of cotton, adsorption hysteresis has always been observed,[3, 4, 5, 6] with the result that there has been a general lack of application of the results obtained with inorganic gels. It is our belief that the behavior of cellulose as an adsorbent is not

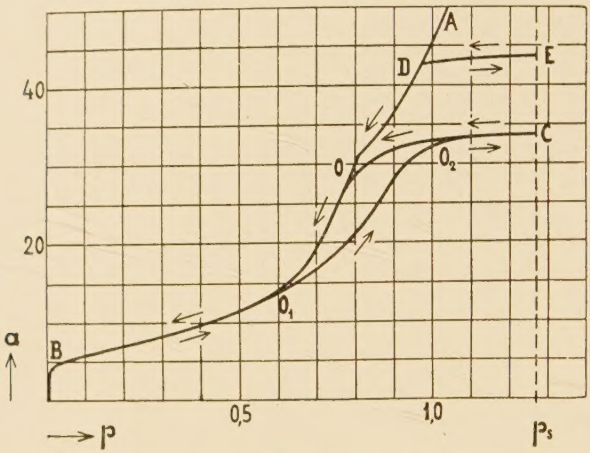

FIG. 1. Adsorption—desorption isotherms of SiO_2-gels. (Taken from H. Freundlich, *Capillarchemie, 2,* 555 (1932).

exceptional, but that it is exceedingly difficult to free it of permanent gases, especially oxygen.

It is therefore the purpose of this study to investigate the adsorption of water vapor by cellulose under conditions that ensure equilibrium.

Description of the Apparatus

The apparatus, as Fig. 2 shows, consists essentially of a sorption chamber, a manometer, a constant-temperature bath, an air-free water still, a MacLeod gauge and a mercury diffusion pump, along with the necessary accessories such as cut-offs, liquid-air traps, etc.

In the earlier experiments, there were three liquid air traps in the high vacuum part of the apparatus. It was necessary to remove these in order to avoid possible contamination of the samples during the measurements by the vapors which would re-evaporate upon the removal of liquid air from the traps. One trap was placed between the diffusion pump and the cut-off next to the high vacuum side.

The liquid-air traps, to facilitate cleaning, were equipped with a ground-glass joint sealed by mercury. They were tested to determine whether

there was any leakage of gas through the joint, and whether a liquid with a low vapor pressure which would wet the glass wouldn't seal better than mercury. The earlier set up with three traps of this type increased in pressure from a vacuum which no longer could be read by a MacLeod gauge to about 10^{-4} mm. of mercury in five days. This indicates that this type of trap does not permit appreciable leakage. Further, the use of mercury in glass barometers and cut-offs may be cited as a further indication that there is no leakage of gas past a mercury glass contact. To check the second point dibutyl phthalate was placed in the cup above the ground-glass joint, and with the system at a pressure of 1 mm. of mercury, about 1 ml. seeped through in five days.

The MacLeod gauge was calibrated by the Division of Weights and Measures of the National Bureau of Standards and was marked for reading

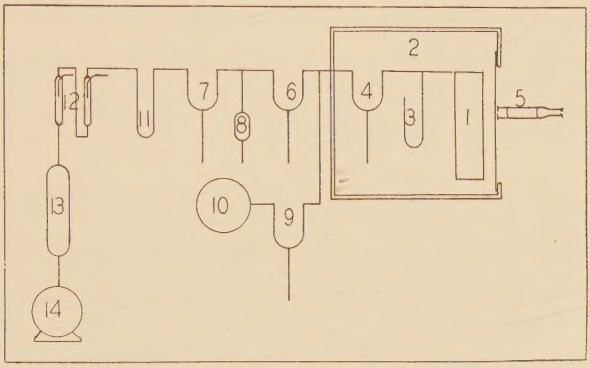

FIG. 2. Sketch of the apparatus finally used. 1, Sorption chamber; 2, Constant temperature bath; 3, Mercury manometer; 4, 6, 7, 9, Mercury cut-offs; 5, Micrometer microscope; 8, MacLeod gauge; 10, Air-free water still; 11, Liquid air trap; 12, Stimson two-stage diffusion pump; 13, Fore vacuum chamber; 14, "Hyvac" fore vacuum pump.

of 10^{-2}, 10^{-3} and 10^{-4} mm. of mercury pressure. Lower pressures could be estimated.

In the first experiments a still designed by Hibben[7] was used to remove permanent gases from water by freezing and subliming the water at liquid air temperatures. This still, however, had two disadvantages, namely: it required the use of liquid air on the high vacuum side of the apparatus and, secondly, it was too expensive to operate. A Taylor type[2] of still, which had been found satisfactory in the experiments on silica gel, was substituted.

A constant-temperature air bath made of a wooden box with necessary doors and windows in which the temperature could be maintained to within $\pm$ .04° C. was used. This bath enclosed the sorption cell, the manometer and the cut-off which separated this part of the system from the rest. The thermometers used in temperature readings were checked by the Heat Division of the Bureau, and were proven adequate for the needs of these

experiments. A constant-recording thermometer was kept within the bath to keep a check on the temperature at all times.

A mercury manometer of the U-type was used to measure the vapor pressures. This manometer had been filled in the same apparatus and under identical conditions for filling barometers at this Bureau. A micrometer vernier-screw arrangement was designed and built in the Bureau shops for reading the vapor pressures as shown by the manometer. This screw was graduated in hundredths of a millimeter.

In the earlier experiments the samples were placed in a series of glass bulbs attached to the apparatus. When, under certain conditions, equilibrium had been apparently reached as indicated by manometer readings, a bulb was sealed off. The weight of the sample and its water content were determined later. This arrangement had several disadvantages, namely: information could be gained about the sample for only those conditions at which the bulb had been sealed off; the manometer was the only check on the equilibrium, and there was danger of losing some of the glass when the bulb was opened.

The sorption chamber used by other investigators appeared to be free from these disadvantages. Therefore it was adopted for our final experiments. However, the sorption chamber was modified to fit our needs. Fig. 3 is a photograph of the sorption chamber used. As can be seen from the

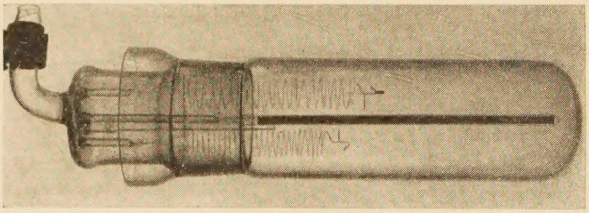

FIG. 3. Sorption chamber. Top is at left.

figure, it consists of an upper part, from the inside of which is suspended two quartz-fibre balances of McBain type,[8] a scale and a thermometer well, and a lower part ground to fit on the upper part. The cup on the lower part is to hold mercury for a seal over the ground-glass joint. The quartz-fibre balances are suspended from hooks on the upper part. The small pyrex glass hook on the bottom of the balance is for holding the sample. The pointer is for reading purposes. The pointer and the hook on the first balance were too heavy. This cut down the useful range of the balance. The heavier pointers and hooks were exchanged for some considerably lighter, and the useful range of the balance was increased up to 50% in some instances. The pointers were dipped in chloroplatinic acid and heated in the flame to give them a coated tip to help make them more visible.

A micrometer microscope was used to read the changes in length of the quartz-fibre balances. This micrometer microscope had a range of 50 mm. and could be read to .001 of a mm. It was checked by the Division of Weights and Measures of the National Bureau of Standards and found to give reproducible results to .01 mm. In order to increase its range it was mounted on a suitable base by means of which it could be raised and low-

cred. The scale inside the cell was obtained from a broken Beckmann thermometer and enclosed in a pyrex glass shell. The 10° C. lines were about 4.4 cm. apart, and their distances apart were determined within .01 mm. by the Division of Weights and Measures. It was planned to use this scale for a reference when the position of the micrometer microscope was changed.

The balances were calibrated by suspending weights of known value on the balance hooks and reading the corresponding elongations. The weights value had been determined by the Division of Weights and Measures to within .0001 gram. The calibration of the balances was made at 4 to 5 mm. pressure and at the same temperature at which the measurements were made.

Experimental Work

Twelve liters of double distilled water were treated with about 100 grams of NaOH and 175 grams of $KMnO_4$. This solution was heated for several days on a steam bath, and stored for three years. This solution was introduced into an all pyrex glass distillation apparatus and slowly distilled. The first portion of water coming over was discarded and the distillation stopped before all the water had distilled over. This water was redistilled over laboratory-distilled C. P. sulfuric acid, again discarding the first and last distillate. This double-distilled water was again distilled and then introduced into the air-free water still.

Unbleached cotton cheese cloth was selected as the adsorptive material for these experiments. To purify the cheese cloth without altering its physical characteristics, it was desized by an enzyme preparation (Rapidase). At the end of this treatment it gave a negative test for starch with iodine. The enzymes and the decomposition products were washed from the cloth by distilled water. Next, the cloth was rinsed several times in redistilled ethyl alcohol, and then extracted for 15 to 20 hours in a Soxhlet apparatus by alcohol, followed by a similar extraction with anhydrous ethyl ether. When this last extraction was completed, the cloth was air-dried and rinsed several times in alcohol to remove the greater portion of the ether. Then it was again extracted for 15 to 20 hours with alcohol. Following the alcohol extraction, it was exposed to the air, so most of the alcohol could evaporate, rinsed several times with special triple distilled water. Next, it was extracted with similar water for about two weeks. The water used for the extraction was replaced several times with fresh distilled water. The solvents in contact with the cotton during the last two extractions were kept near their boiling points.

The glass parts of the apparatus were cleaned by chromic-acid cleaning solution, washed out by tap water, followed by distilled water. In order to remove the last traces of grease, the parts were washed with redistilled ethyl alcohol followed by redistilled C. P. benzene. The apparatus was dried, and assembled, using city gas and oxygen in making all glass joint seals. All necessary blowing, in making the joints, was done through an ascarite absorbent cotton blowing tube. Mercury purified by Hullett's method was used in the MacLeod gauge, and acid, water washed and dried mercury in the cut-offs and the Stimson pump.

To prevent possible photochemical decomposition of the cellulose[9] the sorption chamber and the tube connecting it to the vacuum system were covered with friction tape, except a space through which readings were to be taken. This space was coated with an orange-colored transparent lacquer.

The purified cotton sample was suspended from one of the quartz spirals and the outer part of the sorption chamber was put in place. The entire system was tested for leaks, and, when it was determined that there were no leaks, the pure water was introduced into the air-free water still. The system was then sealed and pumped out to the lowest pressure obtainable with the hyvac pump. Now, the air-free water still was shut off by the cut-off in front of it from the other part of the system. This part of the system was pumped out by the diffusion pump so that it would hold a click vacuum overnight. The air from the water was removed by boiling and intermittently pumping out the air thus liberated. This process was continued for a sufficiently long period to assure complete removal of the air. It was necessary to close off the sorption chamber from the rest of the system during the removal of the gases from the water.

Next, the permanent gases were swept out of the sample and the system by running air-free water vapor into them and pumping this water out of the system along with the liberated air. It was necessary to repeat this operation a large number of times, and also keep the water free from air by running the air-free water still frequently. When the system was swept out a sufficient number of times and the pressure was reduced low enough by pumping, the system was tested to determine the rate of increase of pressure. This was checked three to four times, and it was found in each instance that the pressure increased from a click vacuum to 10^{-4} mm. of mercury in 14 days. It was felt that, under these conditions, satisfactory measurements could be made. Therefore, the system and sample were again swept out with air-free water and pumped out until the permanent gases were eliminated as far as possible.

Measurements were started by taking readings of the manometer, temperature, and the extension of the quartz-fibre balance. Next, a small amount of water vapor was admitted and readings taken when equilibrium was reached. This process was repeated several times and then the water was removed in several successive steps, readings being made at each step. The system and sample were again swept and pumped out and another series of observations made in like manner. This was repeated. The results of these observations of the adsorption—desorption of water by cotton in the absence of permanent gases are shown in Fig. 4.

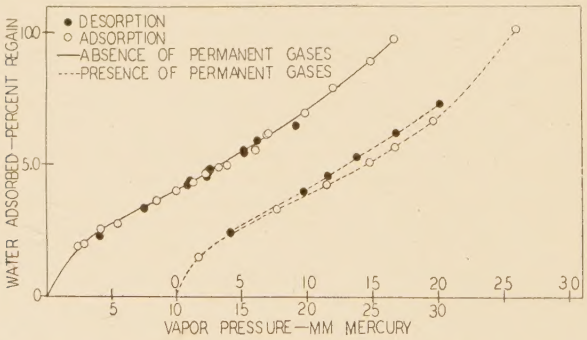

FIG. 4. Relation of the vapor pressure to the amount of water adsorbed. Results of three experiments.

Next, air was let into the system and permitted to remain for several days. The system and sample were then superficially pumped out until a click vacuum was obtained. The apparatus was allowed to stand for a day or so until the pressure had increased to about 10^{-4} mm. of mercury. Then measurements were made in a way similar to those just noted. The results of these observations of the adsorption—desorption of water vapors by cotton cellulose in the presence of permanent gases are also shown in Fig. 4.

All measurements were made at 29.05 ± .04° C. A temperature recorder was kept in the constant-temperature bath, and no readings were taken unless this recorder showed a constant temperature had been maintained for a long enough period to reach equilibrium. The temperature was read twice during the making of any given observation. All vapor pressure readings were made by the mercury manometer and could be duplicated within ± .03 mm. of mercury. Three readings were made of the extension of the spiral at each vapor pressure by the micrometer microscope. These readings check within .01 mm. which corresponds to a variation of less than one-half percent of the weight of the least amount of water adsorbed. The weight of the cotton sample used in these experiments was .0503 gram.

Discussion of Results

It is apparent that there are no marked breaks or discontinuities in the adsorption curve except in the very beginning of the measurements. In as much as there is general agreement as to the presence of a uni-molecular layer of adsorbed vapor, it is not surprising to observe a different trend in the course of the adsorption in the initial stages. While it is true that we have no definite information as to the surface exhibited by a unit weight of cellulose, there is little doubt that this surface is not sufficiently large to account for all the adsorbed water in the form of a uni-molecular layer. Since the total surface of silica gel is undoubtedly greater than that of cotton, and only 3% of the total water adsorbed by silica gel can be accounted for by a uni-molecular layer, it is probably safe to assume that the uni-molecular layer is only sufficient to account for the first few percent of the adsorbed water.

The possibility of the retention of the water by chemical combination or hydration of the cellulose must next be considered. If definite components or hydrates are formed their presence should be indicated by constancy of pressure over the range of the stable hydrate. Our measurements show no indication of such behavior.

If we still persist in the idea of chemical combination as an explanation of the retention of water, it therefore becomes necessary to postulate the existence of a whole series of hydrates. On the other hand, if other vapors such as benzene, carbon tetrachloride, alcohol, etc. should show a similar behavior as water, then the chemical combination explanation must be definitely abandoned. This latter state of affairs is exemplified by the inorganic gels, and there is little reason to doubt that cellulose would behave the same.

It is customary to assume the existence of a thick poly-molecular layer of adsorbed material to account for the retention of adsorbed vapor in excess of the uni-molecular layer. This view we hold to be erroneous on

the basis of the crucial experiments performed by Frazer, Patrick, and coworkers.[10, 11] Furthermore, a large mass of theoretical evidence has been accumulated against the idea of a poly-molecular adsorbed layer.

There still remains the possibility of explaining the magnitude of the adsorption based on the idea of capillary condensation. The application of surface energy considerations to explain the retention of water by porous bodies was first advanced by Friedel,[12] and later extended by Zsigmondy.[1] The essence of the idea is found in the thermodynamic fact that a liquid may be in equilibrium with its vapor at other than the normal vapor pressures provided the pressure on the liquid is different from the vapor pressure. The relation between the hydrostatic pressure on a liquid and its vapor pressure is given by the usual equation

$$vdp = VdP$$

where the left side represents the volume of the liquid and its change of hydrostatic pressure, while the right side refers to the gaseous volume and its change of pressure. If we assume that the vapor obeys the gas law, that the volume of the liquid is constant and that dp equal $2\sigma/r$ where σ = surface tension and r is the radius of curvature of the liquid, then the integration of the above equation leads to the well-known Kelvin relationship:

$$\ln \frac{p}{po} = -\frac{2\sigma M}{RTdr}$$

If we calculate the vapor pressure of water in a tube of radius of 10^{-7} cm. at 29° C. we find it to be 10 to 11 mm. That is to say, in order to account for the retention of water on the basis of the ordinary capillary relationship it becomes necessary to assume radii of molecular dimensions or less. We are therefore faced with a clear reductio ad absurdum.

However a closer examination of the initial postulates made in the integration of our thermodynamic equation, reveals the distinct possibility of extending the range of the capillary concept. It is not sound to assume that the density of a liquid in very small tubes is that of the normal liquid. Furthermore, it is questionable whether the surface tension of a liquid is independent of the radius as assumed. Along such lines as these do we believe it possible to present a complete mechanism for the retention of vapors by porous bodies such as cellulose and the like.

Work is now in progress to modify the Kelvin capillary relationship so as to extend its application and to make it more accurately reflect experimental measurements. It is our belief that this idea, together with an initial mono-molecular adsorbed layer, will faithfully reflect the complete course of the adsorption of vapors by porous bodies. It is perhaps unnecessary to say that these ideas are limited to the adsorption of vapors or gases in the absence of specific chemical or adsorption effects. In other words, it is clearly recognized that there are many types of adsorption that do not come under the scope of these ideas.

Conclusions

(1) Measurements of the adsorption and desorption of water vapor by cellulose are described under conditions that have completely eliminated the phenomenon of hysteresis.

(2) The theoretical aspects of these new results were briefly discussed and provisional suggestions made for the extension of the problem.

The authors wish to express their appreciation to W. E. Emley, Chief of the Organic and Fibrous Materials Division of the National Bureau of Standards, for his interest and co-operation, to S. F. Acree for helpful suggestions, to E. O. Sperling for suggestions on the design of the apparatus, and to the National Bureau of Standards for opening its many facilities to them.

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Biography

THE author was born on January 18, 1903, at St. Paul, Minnesota. He received his elementary education at the St. Paul public schools from September, 1909, until February, 1917, and his high school education at the St. Paul public high schools from February, 1917, until January, 1921. From June, 1920, until January, 1921, he was employed as laboratory helper at the Minnesota State Dairy and Food Commission Laboratories. He entered the University of Minnesota in January, 1921, and was graduated in June, 1925, as Bachelor of Science in Chemistry. In his last school year, he was elected to Phi Lambda Upsilon, honorary chemical fraternity. He was employed as Chemist by the American Linseed Company, St. Paul, Minnesota, from July, 1925, until April, 1926. At this time he received an offer from the National Bureau of Standards which he accepted. In September, 1927, he entered George Washington University, and received a Master of Science degree in Chemistry in June, 1928. During the 1927–1928 school year he was employed by the university as laboratory fellow in inorganic and organic chemistry. He became a member of Alpha Chi Sigma, professional chemical fraternity, in May, 1928. He enrolled in the school of higher studies at the Johns Hopkins University in September, 1928. He was elected to membership in the Philosophical Society of Washington, D. C., in 1930. Due to insufficient funds, he was furloughed by the National Bureau of Standards. He resigned in good standing from this Bureau to accept a position as analyst with the Washington Naval Gun Factory in October, 1933.

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